Ion–Solvent Interaction. The Effect of Added Polar Aprotic Solvents on the Conductances of Tertiary Ammonium Salts in *o*-Dichlorobenzene at 25°[1]

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Abstract: The effects of adding small quantities (*ca.* 0.01 *M*) of acetone, *N,N*-dimethylacetamide, *N*-methylacetamide, dimethyl sulfoxide, and hexamethylphosphoramide on the conductances of dilute solutions (*ca.* 10^{-4} *M*) of the tertiary ammonium salts, *N,N*-dimethyloctylammonium picrate, tri-*n*-butylammonium picrate, and *N,N*-dimethylbenzylammonium picrate, and of the quaternary ammonium salt, tetra-*n*-butylammonium picrate in *o*-dichlorobenzene solvent, have been measured at 25°. The effects of adding *N,N*-dimethyloctylamine to its picrate salt in *o*-dichlorobenzene have been measured. The effects of added benzonitrile and tetramethylene sulfone (sulfolane) on the conductances of solutions of tri-*n*-butylammonium picrate in *o*-dichlorobenzene have been measured at 25°. Values of cation–ligand association constants, K_1^+, are derived from these data. For a given tertiary ammonium ion, the order of decreasing affinity of the ligands for the cations is hexamethylphosphoramide > dimethyl sulfoxide > *N,N*-dimethylacetamide > *N*-methylacetamide > acetone. The affinities of the tertiary ammonium cations for the polar solvents as ligands decrease in the order dimethylbenzylammonium > dimethyloctylammonium > tributylammonium. The affinities of the tertiary ammonium cations for the ligands are several orders of magnitude greater than the affinity of tetra-*n*-butylammonium ion for the same ligands. The addition of benzyldimethylamine had almost no effect on the conductance of its picrate in either methyl ethyl ketone or in nitrobenzene as solvent. The cation–ligand association constants of tri-*n*-butylammonium cation are found to correlate quite well with the corresponding hydrogen-bond formation constants of the ligands with *p*-fluorophenol and with solvent activity coefficients for Na^+ in the ligands as solvent. The significance of these correlations is discussed.

Dipolar aprotic solvents and polar protic solvents frequently display very different salt solubilities and ion reactivities[2–4] and acid–base properties[5,6] even for a pair of solvents of the same polarity (dielectric constant). These differences have been discussed in terms of medium effects or thermodynamic functions of transfer of single ions from one solvent to another;[2–7] for instance, attempts are made to establish measures of the free energy of transfer of a mole of Na^+ from pure solvent 1, S_1, to solvent 2, S_2

$$Na^+(S_1) \longrightarrow Na^+(S_2) \qquad (1)$$

Studies have been carried out in this laboratory of the formation of 1:1 complexes between tertiary ammonium cations, BH^+, and a number of Lewis bases, L, in relatively inert solvents such as *o*-dichlorobenzene (DCB).[8–11]

$$BH^+ + L \rightleftharpoons BH^+,L \qquad K_1^+ = [BH^+,L]/[BH^+][L] \qquad (2)$$

Our experimental approach is based on the measurement of the increased conductivity observed when added Lewis base molecules capture cations from a salt highly associated into ion pairs. We thought it would be of interest to determine cation–ligand complex formation constants using dipolar aprotic and protic substances as ligands. This would establish the relative affinities of these molecules as ligands for tertiary ammonium ions under circumstances where effects due to changes in bulk solvent are minimized. The relative importance of short-range specific ion–solvent interaction might thus be assessed.

Accordingly, we report here the results of measurements of the effects of added hexamethylphosphoramide (HMPT), dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide (DMA), *M*-methylacetamide (NMA), acetone (Me_2CO), and tetramethylene sulfone (sulfolane, TMS) on the conductivities of dilute (10^{-4} *M*) solutions of tri-*n*-butylammonium picrate (Bu_3NHPi), dimethyloctylammonium picrate, ($OctylMe_2NHPi$), and benzyldimethylammonium picrate ($BzMe_2NHPi$) in *o*-dichlorobenzene (DCB) solvent at 25°.

These results will first be compared to recent measurements of hydrogen-bonded complex formation of Taft and coworkers.[12,13] Then note will be taken of the lack of correlation of these results with measures of basicity in the Brønsted sense.[14] Finally, the present results will be compared with measures[15] of the free energy of transfer corresponding to processes represented by eq 1.

Experimental Section

Purification of Chemicals. *o*-Dichlorobenzene (Dow Chemical Co.) was purified as before.[8] Prior to each use the solvent was passed through a 2 × 30 cm column of fired alumina topped with 5

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[2] A. J. Parker, *Quart. Rev., Chem. Soc.*, **16**, 263 (1962).

[3] A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

[4] R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Amer. Chem. Soc.*, **94**, 1148 (1972).

[5] R. G. Bates in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 2.

[6] C. D. Ritchie, ref 5, chapter 4.

[7] For an extensive review see O. Popovych, *Crit. Rev. Anal. Chem.*, **1**, 73 (1970).

[8] E. R. Ralph and W. R. Gilkerson, *J. Amer. Chem. Soc.*, **86**, 4783 (1964).

[9] W. R. Gilkerson and J. B. Ezell, *ibid.*, **89**, 808 (1967).

[10] J. B. Ezell and W. R. Gilkerson, *J. Phys. Chem.*, **72**, 144 (1968).

[11] H. B. Flora, II, and W. R. Gilkerson, *J. Amer. Chem. Soc.*, **92**, 3273 (1970).

[12] D. Gurka and R. W. Taft, *ibid.*, **91**, 4794 (1969).

[13] L. Joris, J. Mitsky, and R. W. Taft, *ibid.*, **94**, 3438 (1972).

[14] E. M. Arnett and E. J. Mitchell, *ibid.*, **93**, 4052 (1971).

[15] R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *ibid.*, **90**, 5049 (1968).

cm of Linde molecular sieve, type 4A. The specific conductance of the solvent was checked prior to each use. A sample of *o*-dichlorobenzene having a specific conductance of about 5×10^{-11} mho/cm was considered a good solvent.

Methyl ethyl ketone (Columbia Organic Chemicals Co.) was twice distilled (bp 79.4° (1 atm)) with the middle fraction being collected each time. The solvent was then stored over molecular sieve (Linde type 4A). Prior to each use the methyl ethyl ketone was treated just as the *o*-dichlorobenzene. The specific conductance of the pure solvent was found to be in the range of 1.5×10^{-8} mho/cm.

Nitrobenzene (Columbia Organic Chemicals Co.) was purified as before.[10] The specific conductance of this solvent was about 1×10^{-10} mho/cm. Tri-*n*-butylammonium picrate was prepared and purified as before.[8]

Tetra-*n*-butylammonium tetraphenylborate was prepared by the addition of equimolar quantities of tetra-*n*-butylammonium iodide (Columbia Organic Chemicals Co.) in aqueous solution to an aqueous solution of sodium tetraphenylborate (Aldrich Chemical Co.). The precipitate which formed was filtered and then recrystallized from a 3:1 mixture of acetone and water. After drying under vacuum the product had a melting point of 234° (lit.[16] mp 235°).

N,N-Dimethyl-*n*-octylammonium picrate was prepared from freshly distilled *N,N*-dimethyl-*n*-octylamine (K & K Laboratories) and picric acid (J. T. Baker Chemical Co.) in a manner analogous to that of the tri-*n*-butylammonium picrate. Effective recrystallization was obtained from a 3:1 mixture of hexane and ethanol, mp 69.5°.

N,N-Dimethylbenzylammonium picrate was prepared from the amine (Aldrich Chemical Co.) and picric acid (J. T. Baker Chemical Co.) in the same manner as the tri-*n*-butylammonium picrate, mp 97° (lit.[17] mp 96°).

Tetra-*n*-butylammonium picrate was obtained from H. B. Flora of this laboratory. The salt was recrystallized from a 3:1 mixture of hexane and ethanol. The melting point of the product after drying under vacuum for several hours was found to be 89° (lit.[18] mp 89.8°).

The distillations required in the following purifications were all performed immediately prior to use in the experiments. Acetone (J. T. Baker Chemical Co.) was stored over molecular sieve (Linde type 4A) for several days and then twice distilled at atmospheric pressure, collecting the middle fraction each time, bp 57°. *N,N*-Dimethyl-*n*-octylamine (K & K Laboratories) was purified by vacuum distillation on a 2 × 30 cm Vigreux column. The middle fraction boiling at 85° (11 mm) was collected. Dimethyl sulfoxide (J. T. Baker Chemical Co.) was dried over molecular sieve (Linde type 4A) overnight and then vacuum distilled from calcium hydride on a 2 × 30 Vigreux column. The center fraction boiling at 53° (5 mm) was collected. *N,N*-Dimethylacetamide (Aldrich Chemical Co.) was vacuum distilled on a 2 × 30 cm Vigreux column. The center fraction boiling at 48° (18 mm) was collected. Hexamethylphosphortriamide (Matheson Coleman and Bell) was dried over molecular sieve (Linde type 4A) for several days and then vacuum distilled on a 2 × 30 cm Vigreux column. The middle fraction boiling at 79° (7 mm) was collected. *N*-Methylacetamide (Aldrich Chemical Co.) was vacuum distilled on a 2 × 30 cm Vigreux column. The center fraction was collected. Because of the rapid decomposition of this material the sample was collected as a solid (the collection flask cooled) and melted only when necessary for the preparation of solutions. All transfers of this material were made using a glass hypodermic syringe. *N,N*-Dimethylbenzylamine (Aldrich Chemical Co.) was vacuum distilled on a 2 × 30 cm Vigreux column collecting the middle fraction which boiled at 60° (14 mm).

Preparation of Solutions. Each salt was dried overnight under vacuum before use. The salts were then transferred in the drying pistol to a nitrogen filled drybox. In the drybox the salt was weighed into a platinum crucible on a 0.1-mg analytical balance. After weighing, the salt was transferred to a flask and the crucible rinsed with a small portion of the solvent. Final weighing of the solution was made on a large capacity 1.0-mg analytical balance located outside the drybox. The salt concentration in a typical experiment was about 10^{-4} *M*.

The ligand solutions were also prepared by weight. Because these ligands are all liquids at room temperature, they were weighed on a 0.1-mg analytical balance outside the drybox. A glass hypodermic syringe was used in the transfers to minimize the contact between the ligands and the air. The solvent used in the preparation of the ligand solutions was a portion of the salt solution which was prepared as described above. This was done so that the salt concentration would remain constant throughout the experiment. The ligand solution concentration in a typical experiment was about 10^{-2} *M*.

Conductance Measurements. The conductance cells used in this work were both of the Kraus (erlenmeyer) type with bright platinum electrodes. One cell was prepared specifically for this laboratory and had a cell constant of 0.02000 cm^{-1} (±0.2%). The other (Beckman Instruments Co.) had a cell constant of 0.2817 cm^{-1} (±0.2%). Both cells were calibrated several times at various intervals in this work using tetra-*n*-butylammonium tetraphenylborate in *o*-dichlorobenzene by comparison of the experimental conductances of solutions of the salt with the results of Zwolenik and Fuoss.[16] The conductance bridge and thermostat have already been described.[8,19]

The experimental procedure used in carrying out the titrations of salt solution with ligand-in-salt solution has already been described.[11]

The physical constants of the solvents at 25° necessary in treatment of the data are given in the order dielectric constant, density (grams per cubic centimeter), and viscosity (centipoise): $PhNO_2$,[20] 34.69, 1.1977, 1.839; DCB, 10.06,[21] 1.3007,[8] 1.272.[22]

Results

Values of the molar conductivity, Λ, for the salt solutions without added ligand and values of $R = \Lambda_L^2/\Lambda^2$, the ratio of the square of the molar conductivity Λ_L in the presence of ligand to the square of the molar conductivity in the absence of ligand, appear in Table IV in the microfilm edition of this journal,[23] for the salts and ligands in *o*-dichlorobenzene. Values of Λ at various salt concentrations for $BzMe_2NHPi$ in $PhNO_2$ with and without added $BzMe_2N$ appear in Table V in the microfilm edition.[23] We have previously shown[8-11] that conductivity increases occurring upon the addition of Lewis bases to tri-*n*-butylammonium picrate solutions in DCB were due to the association of the cation with a molecule of Lewis base to form a 1:1 cation–ligand complex, eq 2. It will be shown that ion–ligand complex formation can account for the increased conductances reported here. In the discussion which follows we shall be interested in the ratio K/K_0, where K is the apparent ion pair dissociation constant in the presence of ligand and K_0 is that in the absence of ligand.

The relation of the experimental values of molar conductivity (and of the ratio R) to the ratio K/K_0 is reasonably straightforward. The tertiary ammonium salts are highly associated into ion pairs, BH^+Pi^-, in DCB, even at 10^{-4} *M*. The ion pair dissociation constants of these salts are in the neighborhood of 3×10^{-10} M^{-1}.[8] The dissociation equilibrium is represented by eq 3. Here $[BH^+,Pi^-]$ is the molar concentration of ion pairs whose activity coefficient is taken to be unity, and $y_\pm$ is the mean molar ionic activity coefficient, taken to be given by a form of the Debye–

$$BH^+,Pi^- \rightleftharpoons BH^+ + Pi^- \qquad K_0 = [BH^+][Pi^-]y_\pm^2/[BH^+,Pi^-] \quad (3)$$

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[16] J. J. Zwolenik and R. M. Fuoss, *J. Phys. Chem.*, **68**, 903 (1964).

[17] J. V. Brown, M. Kuhn, and O. Goll, *Ber.*, **59**, 2335 (1926).

[18] H. L. Curry and W. R. Gilkerson, *J. Amer. Chem. Soc.*, **79**, 4021 (1957).

[19] J. B. Ezell and W. R. Gilkerson, *J. Phys. Chem.*, **68**, 1581 (1964).

[20] H. Sadek and R. M. Fuoss, *J. Amer. Chem. Soc.*, **76**, 5905 (1954).

[21] P. H. Flaherty and K. H. Stern, *ibid.*, **80**, 1034 (1958).

[22] F. Accascina, E. L. Swarts, P. L. Mercier, and C. A. Kraus, *Proc. Nat. Acad. Sci. U. S.*, **39**, 917 (1953).

[23] See paragraph at end of paper regarding supplementary material.

Hückel limiting law.[24] The Shedlovsky conductance equation,[25] which is applicable when ion association is large,[24] may be put into the form

$$K = (\Lambda S/\Lambda_0)^2 C y_\pm^2/(1 - \Lambda S/\Lambda_0) \qquad (4)$$

Note that the quantity $\Lambda S/\Lambda_0$ is γ, the fraction of free ions. The factor S is the Shedlovsky function,[25] correcting Λ for ion atmosphere effects. Both S and $y_\pm^2$ are very close to unity at the ion concentrations we deal with here. Typically, the values of molar conductivity Λ range from less than 0.1 to slightly more than 1 ohm^{-1} cm^2 mol^{-1}, while Λ_0 takes on values in the neighborhood of 40. Only in the case of added HMPT are the values of $\Lambda S/\Lambda_0$ for the tertiary ammonium salts large enough that the quantity $1 - \Lambda S/\Lambda_0$ differs from 1 by more than 1%. The limiting molar conductivity of a tertiary ammonium salt in which the cation is complexed with triphenylphosphine oxide (Ph_3PO) has already been shown[10] to be only 10% less than the value of Λ_0 for the uncomplexed salt. We assume here then that the value of Λ_0 for $BH^+,L + Pi^-$ is the same as that for $BH^+ + Pi^-$ for all the ligands and salts. The stoichiometric salt concentration C remains constant during the course of each of the ligand titration experiments (Table IV in the microfilm edition).[23] Then since S and $y_\pm^2$ are so close to unity, and change so slightly during a titration experiment, the ratio K/K_0 becomes

$$K/K_0 = (\Lambda_L/\Lambda)^2/(1 - \Lambda_L/\Lambda_0)$$

or

$$K/K_0 = R/(1 - \Lambda_L/\Lambda_0) \qquad (5)$$

Note that eq 5 reduces to $K/K_0 = R$ for all the titration experiments reported here except for those involving HMPT as a ligand and Bu_4NPi as the salt.

Consider the formation of one or more complexes of ligand with cation, eq 6a and 6b, with the anion, eq 6c, and with the ion pair itself, eq 6d, in addition to ion pair dissociation, eq 3. Macau, Lamberts, and Huyskens[26] have derived an expression, eq 7, for the ratio K/K_0 in terms of the equilibrium constants for the processes postulated in eq 6. The following simplifying situations may arise: (a) the cation–ligand (or anion–ligand) complex, BH^+,L, is the only one of importance, when eq 7 reduces to eq 8; (b) the two cation–ligand complexes, BH^+,L and BH^+,L_2, are the only ones of importance, when eq 7 reduces to eq 9; (c) the cation complex BH^+,L and the anion complex Pi^-,L are the predominant complex species, when eq 7 reduces to eq 10 (of course, a conductivity experiment alone cannot distinguish between case (b) and (c)); (d) the ion pair–ligand complex BH^+,L,Pi^- is important in addition to the cation complex, BH^+,L, when eq 7 reduces to eq 11.

$$BH^+ + L \rightleftharpoons BH^+,L \qquad K_1^+ = [BH^+,L]/[BH^+][L] \qquad (6a)$$

$$BH^+,L + L \rightleftharpoons BH^+,L_2 \qquad K_2^+ = [BH^+,L_2]/[BH^+,L][L] \qquad (6b)$$

$$Pi^- + L \rightleftharpoons Pi^-,L \qquad K_1^- = [Pi^-,L]/[Pi^-][L] \qquad (6c)$$

$$L + BH^+,Pi^- \rightleftharpoons BH^+,L,Pi^- \qquad K_p = [BHLPi]/[BHPi][L] \qquad (6d)$$

$$K/K_0 = (1 + K_1^+[L] + K_1^+K_2^+[L]^2)(1 + K_1^-[L])/(1 + K_p[L]) \qquad (7)$$

$$K/K_0 = 1 + K_1^+[L] \quad (\text{or } K/K_0 = 1 + K_1^-[L] \text{ in case of the anion}) \qquad (8)$$

$$K/K_0 = 1 + K_1^+[L] + K_1^+K_2^+[L]^2 \qquad (9)$$

$$K/K_0 = 1 + (K_1^+ + K_1^-)[L] + K_1^+K_1^-[L]^2 \qquad (10)$$

$$K/K_0 = (1 + K_1^+[L])/(1 + K_p[L]) \qquad (11)$$

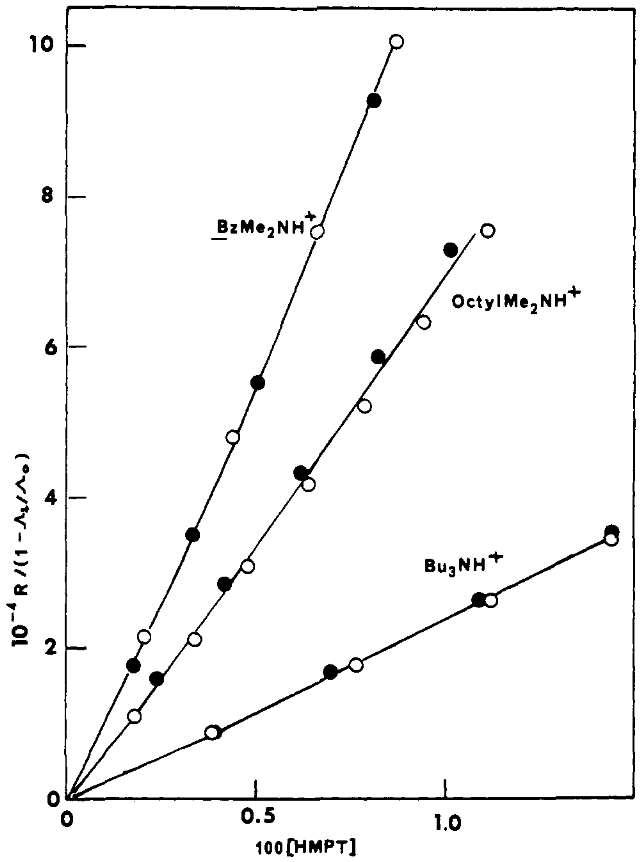

Figure 1. Corrected ratios, $R/(1 - \Lambda_L/\Lambda_0)$, for Bu_3NHPi (○, 0.0943 m*M*; ●, 0.0941 m*M*), $OctylMe_2NHPi$ (○, 0.194 m*M*; ●, 0.195 m*M*), and $BzMe_2NHPi$ (○, 0.209 m*M*; ●, 0.207 m*M*) *vs.* molar concentration of added HMPT in *o*-dichlorobenzene at 25°.

Figure 1 shows the variation of the function $R/(1 - \Lambda_L/\Lambda_0)$ for the three tertiary ammonium salts with the concentration of HMPT in DCB. Independent values of Λ_0 cannot be determined by extrapolation for such weak electrolytes as these salts are found to be. Λ_0 was taken to be 38 for Bu_3NHPi.[8] Λ_0 was estimated to be 41 for $BzMe_2NHPi$ in DCB by assuming the ratio of Λ_0 for this salt to that for Bu_4NPi was equal to the same ratio in $PhNO_2$, where Λ_0 values for both salts can be determined by extrapolation. The following values of Λ_0 were used in these estimates: Bu_4NPi in $PhNO_2$,[27] 27.9, and in DCB,[18] 36.8; $BzMe_2NHPi$ in $PhNO_2$, 30.8 (this work). Λ_0 was taken to be 38 for

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(24) C. DeRossi, B. Sesta, M. Ballistini, and S. Petrucci, *J. Amer. Chem. Soc.*, **94**, 2961 (1972).

(25) T. Shedlovsky, *J. Franklin Inst.*, **225** (1938).

(26) J. Macau, L. Lamberts, and P. Huyskens, *Bull. Soc. Chim. Fr.*, **7**, 2387 (1971). Note that only one kind of ion pair–ligand complex is indicated in eq 6 rather than the two kinds considered by Lamberts and Huyskens. We cannot in a conductance experiment distinguish between the two kinds they postulate.

(27) E. G. Taylor and C. A. Kraus, *J. Amer. Chem. Soc.*, **69**, 1731 (1947).

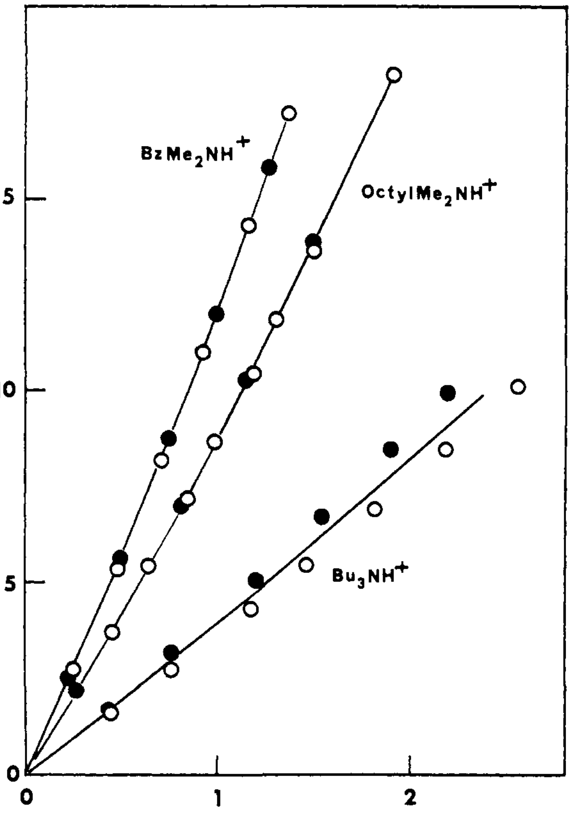

Figure 2. Ratios, R, for Bu$_3$NHPi (○, 0.0925 mM; 0.0946 mM), OctylMe$_2$NHPi (○, 0.197 mM; ●, 0.198 mM), and BzMe$_2$NHPi (○, 0.200 mM; ●, 0.198 mM) *vs.* molar concentrations of added DMSO in *o*-dichlorobenzene at 25°.

OctylMe$_2$NHPi. We are unaware of any reports of values of Λ_0 for this salts in other solvents. At any rate, a change of 3 units of Λ_0 results in at most a change of 1% in the factor $(1 - \Lambda_L/\Lambda_0)$, so that the uncertainty in Λ_0 for this salt is not regarded as serious for purposes of applying the correction in eq 5. Slight upward curvature can be noted in the case of each salt in Figure 1. This is indicative that more than one ligand molecule is interacting with the cation, case b, or another is interacting with the anion, case c. Accordingly, plots of the quantity

$$((R/(1 - \Lambda_L/\Lambda_0)) - 1)/[L]\ vs.\ [L]$$

were made. Taking $R/(1 - \Lambda_L/\Lambda_0)$ to be K/K_0, it may be seen from eq 9 for instance that

$$((R/(1 - \Lambda_L/\Lambda_0)) - 1)/[L] = K_1^+ + K_1^+K_2^+[L]$$

so that the intercept as [L] goes to zero of such a plot yields values of K_1^+. These are tabulated in Table I. Because of the corrections which had to be applied, and ambiguity in the interpretation (case b or c), we do not report values of the slopes of these latter plots, except to note that they are linear and positive.

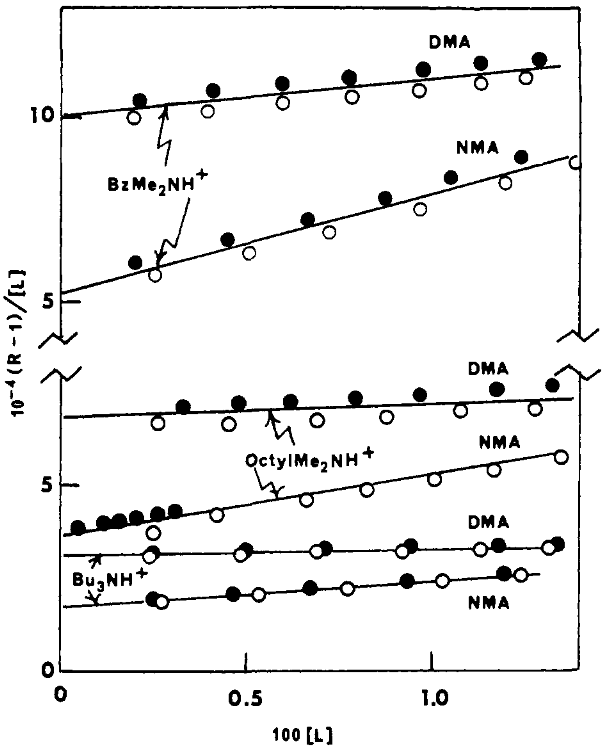

Figure 3. The effects of added NMA and DMA on the conductance of the three tertiary ammonium picrates. The function, $(R - 1)/[L]$, is plotted *vs.* [L], the molar concentration of ligand; 0.199 mM Bu$_3$NHPi was used for both runs each with NMA and with DMA as ligands. With DMA, the concentrations of OctylMe$_2$NHPi used were 0.197 mM (○) and 0.198 mM (●). With NMA the concentrations of OctylMe$_2$NHPi used were 0.0989 mM (○) and 0.197 mM (●). With DMA, the concentrations of BzMe$_2$NHPi used were 0.198 mM (○) and 0.199 mM (●). With NMA, the concentrations of BzMe$_2$NHPi used were both 0.201 mM.

Table I. Cation–Ligand Association in DCB at 25°

Ligand	Cation Bu$_3$NH$^+$	 OctylMe$_2$NH$^+$	 BzMe$_2$NH$^+$	 Bu$_4$N$^+$
	$10^{-3}K_1^+$, M^{-1}			
HMPT[a]	2250 ± 40[b]	6100 ± 200	9700 ± 100	0.022[c]
DMSO[a]	37 ± 3	78 ± 0.5	105 ± 1	0.012
DMA	31 ± 0.7	67 ± 2	101 ± 2	0.008
NMA	18 ± 1	35 ± 0.4	52 ± 3	0.017
Me$_2$CO	0.25 ± 0.01	0.40 ± 0.03	0.52 ± 0.04	0.003
OctylMe$_2$N		2.4		
TMS[a]	0.70 ± 0.01			
PhCN[a]	0.14			

[a] Association constants for these ligands with Bu$_3$NH$^+$ were determined by H. B. Flora, II, in this laboratory. [b] Standard deviations for two or more experiments. [c] Calculated assuming observed increase is due to association of one ion with the ligand.

The ratios R for the tertiary ammonium salts in the presence of added DMSO are shown in Figure 2. These also exhibit slight curvature up, so that plots of $(R - 1)/[L]$ *vs.* [L] were made. The intercepts as [L] goes to zero of these graphs were taken to be values of K_1^+ and are listed in Table I. Figure 3 shows a comparison of plots of $(R - 1)/[L]$ *vs.* [L] for the three tertiary ammonium salts with the two amide ligands, DMA and NMA. Note that for each salt, the intercept as [L] approaches zero is greater for DMA, but the slope is greater for NMA. The significance of the values of the slopes will be discussed below but the intercepts are taken to be values of K_1^+ and are listed in Table I. Figure 4 shows the values of R for the three tertiary ammonium salts in the presence of added acetone. The intercepts as [L] goes to zero of plots of $(R - 1)/[L]$ *vs.* [L] are taken to be values of K_1^+ for this ligand and are listed in Table I. Also listed in this table are values of K_1^+ for OctylMe$_2$N with OctylMe$_2$NH$^+$ and for TMS and PhCN with Bu$_3$NH$^+$. These latter values were obtained in the same manner as those above. An in-

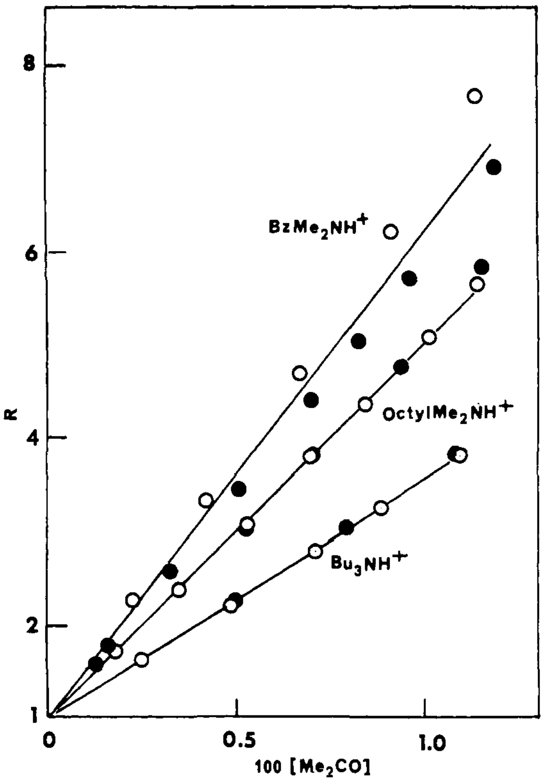

Figure 4. The effects of added acetone on the conductance ratios, R, for the tertiary ammonium salts in *o*-dichlorobenzene at 25°. The concentrations of Bu_3NHPi used were 0.197 mM for both runs. The concentrations of $OctylMe_2NHPi$ used were 0.0992 mM (○) and 0.301 mM (●). The concentration of $BzMe_2NHPi$ used was 0.198 mM for both runs.

dication of the reproducibility of the values of K_l^+ as determined by two different operators at two different times may be obtained by comparison of the value of $K_l^+ = 140\ M^{-1}$ for PhCN with Bu_3NH^+ reported here (H. B. F., 1969) and one previously reported,[9] $K_l^+ = 150 \pm 10$ (J. B. E., 1965).

The addition of the ligands to solutions of the quaternary ammonium salt Bu_4NPi in DCB did result in increased conductivity, albeit small. Figure 5 shows the effect of added HMPT on the ratios R for Bu_4NPi. These ratios, listed in the microfilm edition,[23] were corrected for the changes in the fraction γ of salt dissociated (maximum correction 7%) and the changes in ion atmosphere correction factors S and $y_\pm$ (maximum correction due to both of these factors is 3.5%) using eq 4, to obtain values of K/K_0. These corrected ratios, plotted *vs.* ligand concentration, were all linear and yielded the slopes listed as values of K_l^+ in Table I.

As in the case of the interaction of $OctylMe_2N$ with $OctylMe_2NHPi$ in DCB, an attempt was made to determine a value of K_l^+ for the interaction of *N*,*N*-dimethylbenzylamine ($BzMe_2N$) with *N*,*N*-dimethylbenzylammonium picrate ($BzMe_2NHPi$) in DCB. As the solution containing the amine was added to the pure salt solution, the conductance was found to increase with time indicating a reaction. On addition of larger concentrations of amine, the reaction appeared to proceed faster. From the data it was apparent that if the ion–ligand interaction was present, it was small and being masked by the reaction. To check this observation a small portion of the purified amine was added to a sample of the pure DCB solvent and the conductance monitored for several minutes. The conductance was found to increase with time indicating that the amine was reacting with the solvent. In order to obtain information on this system other solvents were tried.

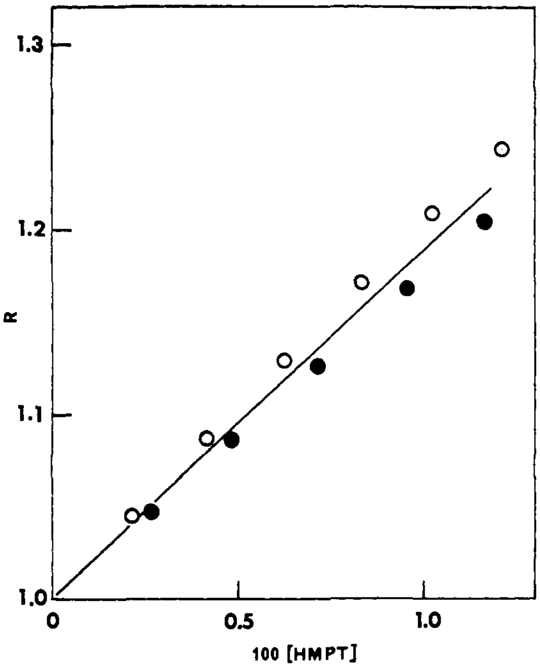

Figure 5. The effect of added HMPT on the ratio, R, for Bu_4NPi in *o*-dichlorobenzene at 25°. The salt concentrations used were 0.203 mM (○) and 0.194 mM (●).

One of these solvents was methyl ethyl ketone (MEK). MEK was chosen primarily because of its ease of purification and because it has been widely used[28] as a solvent in conductance studies. In this experiment it was found that the conductance decreased by 0.4% when a 0.00206 M salt solution was made 0.013 M in amine. Thus, a determination of the value of K_l^+ in this solvent was impossible.

Another of the solvents used in this attempt was nitrobenzene ($PhNO_2$). As in the case of MEK this solvent is easily purified and has been quite widely used in conductance studies. Since $PhNO_2$ is a more polar solvent the ion pair dissociation constants of the trialkyl and aryl ammonium picrates are generally in the range of 10^{-4} to $10^{-5}\ M^{-1}$. The magnitude of these constants makes the use of the titration method used for these salts in DCB of doubtful value; however, the value of K_l^+ may be determined from the ratio of the dissociation constants measured with and without added amine in the system.

To determine the ion pair dissociation constants the Shedlovsky equation, eq 4, was used. The equation was rearranged for these calculations

$$\frac{1}{\Lambda S} = \frac{1}{\Lambda_0} + \Lambda S C y_\pm^2 / K \Lambda_0^2 \qquad (12)$$

where S and $y_\pm$ are functions of Λ, C, and Λ_0 (or K). The calculation requires that either a value of K or of Λ_0 be known. Values of Λ as a function of salt concentration with and without added amine appear in the

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[28] S. Crisp, S. R. C. Hughes, and D. H. Price, *J. Chem. Soc. A*, 603, 1464 (1968).

microfilm edition of this journal.[23] The equivalent conductance at the lowest salt concentration was taken to be the initial trial value of Λ_0 for each set of measurements. The calculations were carried out by computer using a Fortran IV program written for this purpose. Values of Λ_0 and of the ion pair dissociation constant K with and without added amine appear in Table II.

Table II. Conductance Parameters for $BzMe_2NHPi$ in $PhNO_2$ at 25°

$[BzMe_2N]$, M	10^4K, M^{-1}	Λ_0, ohm^{-1} cm^2 mol^{-1}
0.0	1.164	30.79
0.0	1.159	30.84
0.0115	1.174	30.91
0.0537	1.212	30.58

Discussion

Acetone, one of the least effective ligands of those investigated here, has an almost 100-fold greater effect increasing the ion pair dissociation of the tertiary ammonium picrates in DCB than it has on the dissociation of the quaternary ammonium picrate, Bu_4NPi, Table I. If the ligand interacts with both cation and anion, then eq 10 applies. The apparent values of K_1^+ would, in fact, be the sum $K_1^+ + K_1^-$. If all the effects of added ligands on the conductance of Bu_4NPi are attributed to specific interaction of the ligands with the picrate anion, then K_1^- is not large enough in the case of any of the ligands studied here to affect our interpretation of the values of K_1^+ for the tertiary ammonium salts in Table I.

It is true that increases in the dielectric constant of the solutions due to added polar solutes might account for some of the observed effects. Addition of 0.022 M o-dinitrobenzene ($\mu = 6.3$ D) to DCB at 25° has been found[29] to result in an increase in dielectric constant of from 10.06 for the pure solvent to 10.24 for the solution. The ratio of the ion pair dissociation constant of Bu_3NHPi in the dinitrobenzene solution to that in pure DCB has been found[30] to be 1.67. This relatively small increase in K/K_0 for the highly polar but weak Lewis base o-dinitrobenzene is to be compared with the value $K/K_0 = 5.7$ in a 0.022 M solution of acetone,[31] a far less polar molecule ($\mu = 2.85$ D) but a stronger Lewis base. We believe the conductance increases we report here for the tertiary ammonium salts are primarily due to specific ion–ligand interaction, rather than to changes in bulk solvent properties such as the dielectric constant.

The three tertiary ammonium cations show the same order of affinity for the ligands, decreasing in the order $BzMe_2NH^+ > OctylMe_2NH^+ > Bu_3NH^+$, the order presumably reflecting the increasing steric repulsion encountered by the incoming ligands. It may be noted that the ligand association constants for DMA and NMA with the quaternary ammonium salt Bu_4NPi are reversed in the order from that found with the tertiary ammonium salts. We think this is a real effect possibly due to NMA hydrogen bonding to picrate anion. DMA, and the other ligands, would not be expected to hydrogen bond with an acceptor to the same extent as NMA. Further evidence supporting this interpretation may be seen in Figure 3 where we had already noted that the slopes of the $(R - 1)/[L]$ $vs.$ [L] plots were greater for NMA than for DMA with the three tertiary ammonium salts. If NMA is interacting with Pi^- in addition to the cation, then from eq 10

$$(R - 1)/[L] = K_1^+ + K_1^- + K_1^+K_1^-[L]$$

while for the case of a second ligand interacting with the cation, an equation with the same functional dependence on [L] is derived but the interpretation of the parameters must be different, the slopes in this latter case being proportional to K_2^+ rather than K_1^-.

$$(R - 1)/[L] = K_1^+ + K_1^+K_2^+[L]$$

The uncertainty in the experimental data and the small values of the slopes involved make the effort to be more quantitative in a treatment of the possible interaction of NMA with picrate anion of doubtful value.

The magnitude of the value of K_1^+ for $OctylMe_2N$ associating with $OctylMe_2NH^+$ in DCB, Table I, is quite reasonable when compared with other previously determined values of K_1^+ for the interaction of an amine with its protonated cation in this solvent. Ralph[8] reported a value of 560 M^{-1} for Bu_3N with Bu_3NH^+ and a value of 19,000 M^{-1} for pyridine with pyridinium cation.

The attempt to determine the possible effect of added $BzMe_2N$ on the conductance of $BzMe_2NHPi$ in DCB was a failure since it was found that the amine appeared to react with the dichlorobenzene solvent itself. No such reaction was indicated in the case of $OctylMe_2N$ nor with Bu_3N.[8] However, Mixon[32] found that when piperidine was added to pure DCB at 25°, the conductance of the amine solution increased with time, indicating that some reaction was taking place.

The slight decrease in conductance observed when $BzMe_2N$ was added to a solution of its picrate salt in methyl ethyl ketone could be attributed to a rise in the solvent viscosity and thus a decrease in ion mobility. The decrease could also be due to the amine complexing with the free cations in a system where the fraction present as ion pairs is so small that mass action results in little or no net change in the total concentration of free ions due to formation of the cation–ligand complex. The value of Λ_0 for the picrate of the cation–ligand complex of piperidinium ion with piperidine in nitrobenzene has been shown[33] to be 10% less than that of the uncomplexed salt. The small value of the molar conductance, $\Lambda = 2.78$, for the 2.06×10^{-3} M $BzMe_2NHPi$ solution in MEK is taken as an indication that the ions from the salt are paired to a significant extent (Λ_0 is 148 for NaI in this solvent at 25°[28]). The evidence points to the added amine having no tendency to form a complex with its protonated form in MEK solvent. The conclusion is materially the same for this system in $PhNO_2$ solvent. Here enough conductance

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[29] W. R. Gilkerson and K. K. Srivastava, *J. Phys. Chem.*, **64**, 1485 (1960).

[30] E. R. Ralph, III, unpublished work in this laboratory.

[31] From further work on this system in this laboratory by M. L. Junker, Ph.D. Dissertation, University of South Carolina, 1973.

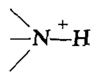
[32] A. L. Mixon, Ph.D. Dissertation, University of South Carolina, 1969.

[33] A. L. Mixon and W. R. Gilkerson, *J. Amer. Chem. Soc.*, **89**, 6410 (1967).

data were taken that the ion pair dissociation constant of this salt could be determined in pure PhNO_2 and in two amine–nitrobenzene solutions as solvent, Table II. The small 4% increase in the ion pair dissociation constant in the presence of 0.0537 M amine could be real, but we shall take it as indicating that little or no specific interaction takes place between BzMe_2N and BzMe_2NH^+ in this solvent as well.

To explain the differences in the observations reported here for BzMe_2N and its cation and for $\text{OctylMe}_2\text{N}$ and $\text{OctylMe}_2\text{NH}^+$, molecular models of BzMe_2N and its cation were prepared along with those of Bu_3N and $\text{OctylMe}_2\text{N}$ and their respective cations. The models for the Bu_3N and $\text{OctylMe}_2\text{N}$ systems indicated that due to the great rotational freedom of the alkyl chains quite close approach between the amine and cation was possible. However, the models for BzMe_2N and its cation indicated that the rigid nature of the aromatic ring prevented a close approach of this amine and its cation. It should be noted that this steric interaction which prevents a close approach to form the complex is only apparent in the case of the free amine interacting with the protonated amine; *i.e.*, this argument does not apply in the case of the amine interacting with the *p*-fluorophenol as reported[12] by Gurka and Taft nor to the interaction of the benzyldimethylammonium cation with the other ligands studied in the present work.

The association constants of ligands with tertiary ammonium cations are all several orders of magnitude greater[8–11,34] than those with quaternary ammonium cations such as Bu_3MeN^+ and Bu_4N^+. The greater affinity of ligands for tertiary ammonium ions may be described[35] as being due to the presence of hydrogen bonding between the



group and the ligand, or it may be ascribed to a shorter distance of closest approach of the negative end of the ligand to the seat of positive charge in the tertiary ammonium ion–ligand complex. A comparison can be made of the values of K_1^+ for the association of tri-*n*-butylammonium cation with a number of Lewis bases in DCB solvent[36] at 25°, eq 2 or 6a, with the equilibrium constants, K_f, for the formation of hydrogen-bonded complexes between *p*-fluorophenol and the Lewis bases in CCl_4 at 25° reported by Taft and Gurka,[12,37] eq 13.

$$p\text{-FC}_6\text{H}_4\text{O-H} + \text{L} \rightleftharpoons p\text{-FC}_6\text{H}_4\text{O-H}\cdots\text{L} \qquad K_f \qquad (13)$$

Values of log K_1^+ for diethyl ether,[11] tetrahydrofuran,[38] acetone (Table I), benzonitrile (Table I), acetonitrile,[8] pyridine,[8] 4-methylpyridine,[8] DMSO (Table I), DMA (Table I), pyridine *N*-oxide,[38] triphenylphosphine oxide,[38] and HMPT (Table I) are plotted *vs.* the corresponding values of log K_f in Figure 6. There is a remarkable correlation between the results of the two kinds of experiments. Note that the line in Figure 6 has a slope of 1.74 and passes through the origin indicating that the free energy changes involved in the association of Bu_3NH^+ with the ligands are almost twice as great as those involved in the formation of the complexes with the phenol.

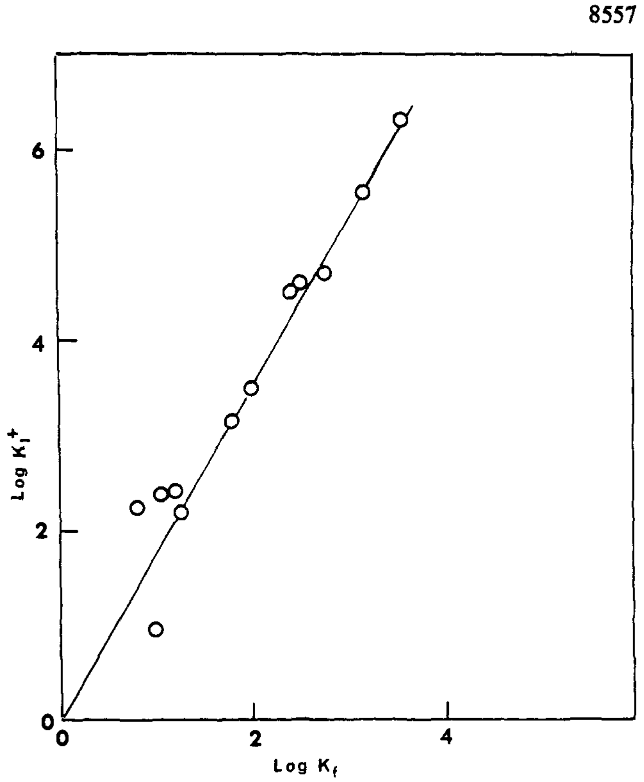


Figure 6. Comparison of cation-complex formation of ligands with Bu_3NH^+ in DCB, measured by log K_1^+, to H-bonded complex formation of ligands with *p*-fluorophenol in CCl_4, measured by log K_f.

In contrast, the lack of correlation between the formation constants for either of these kinds of complexes, $\text{R}_3\text{NH}^+,\text{L}$ or ROH,L, with the pK_a values of the ligands in water or other measures of the ligands as Brønsted bases in proton transfer reactions, has been noted by a number of workers.[9,14,39]

The similarity of the hydrogen-bond interaction in the case of the complex $\text{Bu}_3\text{NH}^+\cdots\text{OPPh}_3$[38] to what might be classed as pure ion–dipole interaction, that between sodium ion and triphenylphosphine oxide (Ph_3PO) in tetrahydrofuran solvent,[40] is striking. In THF at 25°

$$\text{Bu}_3\text{NH}^+ + \text{OPPh}_3 \rightleftharpoons \text{Bu}_3\text{NH}^+,\text{OPPh}_3 \qquad K_1^+ = 230\ M^{-1}$$

while

$$\text{Na}^+ + \text{OPPh}_3 \rightleftharpoons \text{Na}^+,\text{OPPh}_3 \qquad K_1^+ = 250\ M^{-1}$$

This similarity prompts an examination of the relation of the association constants of the ligands with Bu_3NH^+ in DCB to the "solvent activity coefficients"[2–4,15] or the medium effect[7] of the alkali metal ions in dipolar solvents. The "solvent activity coefficient" is related to the difference in the free energy change for some process in one solvent compared to the change in the free energy for the same process in some reference solvent. For ionic systems, an extrathermodynamic

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(34) W. R. Gilkerson and J. B. Ezell, *J. Amer. Chem. Soc.*, **87**, 3812 (1965).

(35) C. R. Witschonke and C. A. Kraus, *ibid.*, **69**, 2472 (1947).

(36) This is the cation–solvent system for which the most information has been accumulated.

(37) Taft has recently reported[13] similar measurements in DCB and other solvents but using fewer Lewis bases. There is a small solvent effect, but it is almost constant for the ligands common to the two studies.

(38) J. B. Ezell and W. R. Gilkerson, *J. Amer. Chem. Soc.*, **88**, 3486 (1966).

(39) H. B. Yang and R. W. Taft, *ibid.*, **93**, 1310 (1971).

(40) H. B. Flora and W. R. Gilkerson, *J. Phys. Chem.*, **77**, 1421 (1973).

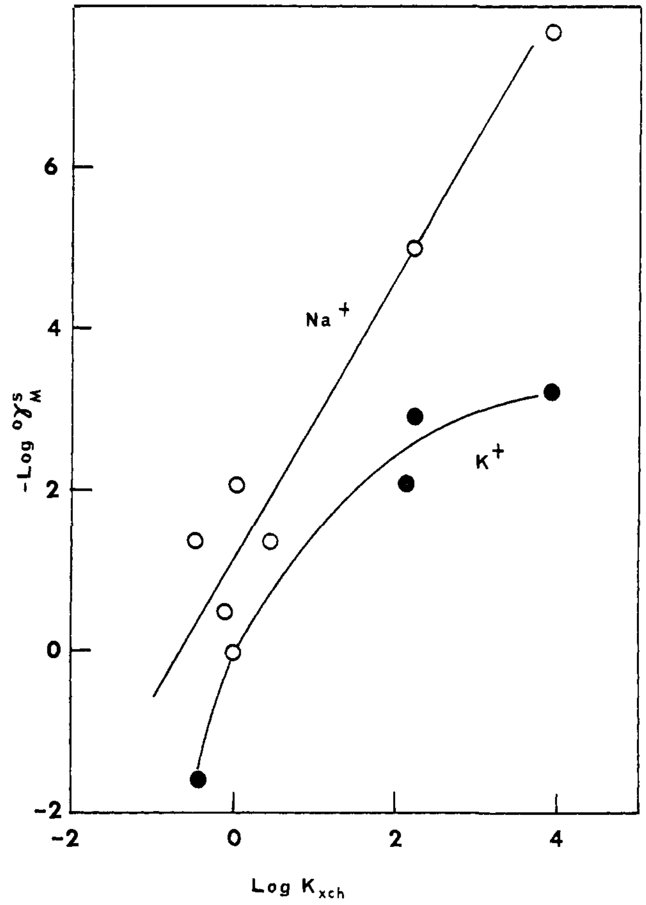

Figure 7. Comparison of "solvent activity coefficients" to equilibrium constants for displacement of solvent molecules as ligands from Bu_3NH^+ in DCB.

assumption is made to enable an assignment of separate portions of the free energy change to each of the ions involved. The variety of processes and extrathermodynamic assumptions have been outlined and discussed by Parker[4,15] and Popovych.[7] In order to be able to compare data for the largest set of ligands (as dipolar solvents) we choose to compare the values of $K_1{}^+$ for ligands with Bu_3NH^+ in DCB at 25° with those "solvent activity coefficients" of Alexander and Parker[15] based on solubilities of salts in several solvents of interest. The processes may be represented by the scheme

$$MX(\text{solid}) \rightleftharpoons M^+ + X^- \text{ (in solvent S)} \qquad K^S$$

$$MX(\text{solid}) \rightleftharpoons M^+ + X^- \text{ (MeCN, reference solvent)} \qquad K^0$$

Then $\log (K^S/K^0) = \log {}^0\gamma^S_{M^+} + \log {}^0\gamma^S_{X^-}$, where $\log {}^0\gamma^S_{M^+}$ is the "solvent activity coefficient" of the ion M^+ in the solvent S referred to the reference solvent (our choice is acetonitrile, MeCN). One of the extrathermodynamic assumptions used by workers in this area,[7] called the TATB assumption by Alexander and Parker,[15] is the one adopted for this comparison. The TATB assumption is that ${}^0\gamma^S_{Ph_4As^+} = {}^0\gamma^S_{Ph_4B^-}$, where Ph_4As^+ is the tetraphenylarsonium cation and Ph_4B^- is the tetraphenylborate anion. $\text{Log}\ {}^0\gamma^S_{M^+}$ is related[41] to the difference between the free energy of the ion M^+ in solvent S and in the reference solvent and should reflect the difference in solvation energy of the ion in the two solvents. The process we shall compare with that represented by $\log {}^0\gamma^S_{M^+}$ is the exchange in the poorly solvating solvent DCB of one molecule of reference solvent, MeCN, for one molecule of solvent S in the complex with Bu_3NH^+, eq 14. Values of $-\log {}^0\gamma^S_{M^+}$

$$Bu_3NH^+,MeCN + S \rightleftharpoons Bu_3NH^+,S + MeCN$$

$$K_{xch} = K_1{}^+(S)/K_1{}^+(MeCN) \qquad (14)$$

for Na^+ and K^+ appear in Table III and are plotted *vs.* values of $\log K_{xch}$ in Figure 7. Also included are values of $-\log {}^0\gamma^S_{Na^+}$ derived from data of Coetzee and coworkers.[42] These latter workers used a different process and extrathermodynamic assumption, but their results are comparable with those of Parker and coworkers. Examination of Figure 7 shows that there is a correlation between the two different measures of ion–solvent interaction. The "solvent activity coefficients" include effects due to a number of solvent molecules interacting with the solute at short range, the interaction of these solvating solvent molecules with surrounding solvent, as well as any contribution due to changes in bulk dielectric constant of the solvent, a Born type term.[40] The equilibrium constants for the exchange of ligands on Bu_3NH^+ in the relatively inert solvent DCB includes effects due principally to specific ion–polar molecule interaction at short range, a contribution due to the difference in the interactions of the two ion–molecule complexes with the surrounding solvent, and a contribution from the difference in interaction of the two ligands with the solvent. The last two contributions are presumed to be small.

Table III. Comparison of Cation–Ligand Exchange in DCB with Solvent Activity Coefficients

Solvent	Log K_{xchg}	$-(\log {}^0\gamma^S_{Na^+})^a$	$-(\log {}^0\gamma^S_{K^+})^a$
HMPT	3.92	7.7	4.8
DMSO	2.22	5.0	4.5
DMA	2.12		3.7^b
Me_2CO	0.03	2.0^c	1.4^c
TMS	0.46	1.4	1.2^c
MeCN	0	0	0
PhCN	−0.14	0.5^c	
MeOH	−0.46	1.4	−1.6

[a] The reference solvent is MeCN here, rather than MeOH. [b] This is the value for dimethylformamide listed by Parker.[15] [c] Coetzee and coworkers.[42]

The similarity of the behavior of Bu_3NH^+ with that of Na^+ toward Ph_3PO as ligand in THF solvent has already been pointed out. Figure 7 shows that the similarity extends to the "solvent activity coefficients" for Na^+, where there is a fairly linear correlation over some seven orders of magnitude in ${}^0\gamma^S_{Na^+}$ and four orders of magnitude in K_{xch}. The slope of the straight line drawn through the point for HMPT in the upper right corner of Figure 7 and the point for MeOH in the lower left is 1.5. If the lower end of the straight line is shifted so that it passes through the point for acetonitrile at the origin, the slope is 2.0. Cogley, Butler, and Grunwald[43] measured cation–ligand association constants for water with (among others) the

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(41) See Popovych[7] for a discussion concerning this relation.

(42) (a) J. F. Coetzee, J. M. Simon, and R. D. Bertozzi, *Anal. Chem.*, 41, 766 (1969); (b) J. M. Simon, Ph.D. Thesis, University of Pittsburgh, 1969, as quoted by Popovych, ref 7.

(43) D. R. Cogley, J. N. Butler, and E. Grunwald, *J. Phys. Chem.*, 75, 1477 (1971).

alkali metal cations Li^+, Na^+, and K^+ in propylene carbonate solvent. They also reported values of free energies of transfer of these ions from water to propylene carbonate. From a plot similar to Figure 7 they estimated that between two and three water molecules were involved in specifically solvating the alkali metal ions. If all the changes in the "solvent activity coefficients" and in the ion–ligand displacement constants in Figure 7 are attributed to specific ion–polar molecule interaction at short range, then the slopes we calculated above imply that one to two molecules of the solvents are involved in the "transfer process" represented by the "solvent activity coefficients." Of course, a more meaningful comparison could be made if cation–ligand association constants were available for these ligands we consider here interacting with Na^+ or Li^+ in a relatively inert solvent. This is an area of research being pursued in this laboratory.

In conclusion, the process involved in specific interaction between tertiary ammonium ions and Lewis bases at short range in solution has been shown to be very similar to that involved in the interaction of alkali metal cations and the molecules of solvent in a number of polar solvents and also to that involved in the formation of hydrogen-bonded complexes between the Lewis bases and *p*-fluorophenol in CCl_4 solvent. Recall that the first and the last of the three processes above do not correlate with measures of proton basicity in the Brønsted sense. It follows then that there is a greater similarity of the energetics of the process of hydrogen-bond formation to the energetics of specific cation–Lewis base interaction than to the energetics of proton-transfer processes.

Supplementary Material Available. Conductance data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8551.

Absolute Temperature Dependence of Chemical Shifts of Lock Solvents. Tetramethylsilane, Hexafluorobenzene, and 1,4-Dibromotetrafluorobenzene

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Abstract: Temperature-dependent studies in nmr have heretofore suffered from the unknown temperature dependence of the reference substance. We have measured the ^{129}Xe resonance frequency in Xe gas extrapolated to zero density using three external references (^1H in TMS and ^{19}F in C_6F_6 and DBTFB) over the range 240 to 440°K. Because of the nature of the isolated xenon atom it should have a rigorously temperature-independent chemical shielding. Hence, the measured temperature dependence is due solely to the external references used. The experimental temperature dependence of chemical shifts for TMS, C_6F_6, and *p*-$C_6Br_2F_4$ reported here provides convenient external references for temperature-dependent studies over the range 240 to 440°K.

In nmr spectroscopic measurements at variable temperatures, the lock solvent or reference substance with respect to which shifts are being measured is itself changing with temperature. This change is generally neglected. Depending on the magnitude of the shifts being measured relative to the magnitude of the reference substance shifts, this could lead to large or small errors in the temperature dependence of interest. The problem is that it is difficult to keep the reference substance at some fixed constant temperature while varying the temperature of the sample. In the use of an internal reference there are two problems. (1) The reference substance would be changing in temperature along with the sample under study. Also, (2) interactions between the reference substance and the sample are very likely temperature dependent. Use of an external reference in a sealed capillary tube or in the outer or inner annular region of coaxial sample tubes eliminates the second problem but not the first.

The temperature-dependent chemical shifts in gases reported by Petrakis and Sederholm were measured relative to CH_4 which was mixed in nearly equimolar amounts with the gases under study.[2] These reported shifts include the intrinsic temperature dependence of methane (temperature dependence of an isolated CH_4 molecule being used as reference) as well as the temperature dependence of the CH_4–CH_4 and CH_4–sample intermolecular interactions. The latter might be negligible since the densities used were quite small (about 5 amagats of each). Even so, one would still need an absolute measure of the CH_4 temperature dependence (due to change in vibrational and rotational averages of chemical shielding with temperature)[3] in order to find the real temperature dependence of the gases of interest. Similarly, Widenlocher measured the temperature dependence of H_2S relative to C_2H_6, HCl, and $(CH_3)_2O$ and CH_3Cl relative to CH_4 in mixtures of

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(1) (a) Loyola University; (b) University of Illinois.

(2) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1174 (1961).

(3) A. D. Buckingham, *J. Chem. Phys.*, **36**, 3096 (1962).